

DEPUTY
TECH DIR W
ACTION W
INFO DOT
FILE W

APR 20 1982
MAY 20 1982

A Contamination Simulation Facility with In-Situ Infrared Analysis Capability

D. J. CARRE , P. D. FLEISCHAUER,
H. R. HEDGPETH, W. J. KALINOWSKI, D. E. MASTURZO,
A. PLUCHINO, and M. A. ROCHA
Chemistry and Physics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

20 January 1982

Property of U. S. Air Force
AEDC LIBRARY
F40600-81-C-0004

C. 2

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Property of U. S. Air Force
AEDC LIBRARY
F40600-81-C-0004

PROPERTY OF U.S. AIR FORCE
AEDC TECHNICAL LIBRARY
ARNOLD AFB, TN 37389

Prepared for
SPACE DIVISION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, California 90009

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER SD-TR-81-91	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) A CONTAMINATION SIMULATION FACILITY WITH IN-SITU INFRARED ANALYSIS CAPABILITY		5. TYPE OF REPORT & PERIOD COVERED
7. AUTHOR(s) D. J. Carré, P. D. Fleischauer, H. R. Hedgpeth, W. J. Kalinowski, D. E. Masturzo, A. Pluchino, and M. A. Rocha		6. PERFORMING ORG. REPORT NUMBER TR-0082(2945-03)-2
9. PERFORMING ORGANIZATION NAME AND ADDRESS The Aerospace Corporation El Segundo, Calif. 90245		8. CONTRACT OR GRANT NUMBER(s) F04701-81-C-0082
11. CONTROLLING OFFICE NAME AND ADDRESS Space Division Air Force Systems Command Los Angeles, Calif. 90009		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE 20 January 1982
		13. NUMBER OF PAGES 23
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Contamination Polyacrylate Solithane 113/300 Fourier transform infrared Polysiloxane 3M No. 465 Transfer Tape Internal reflection spectroscopy Polyurethane Volatile condensable materials Outgassing RTV 560		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A new volatile condensable materials (VCM) facility has been constructed. The facility features a unique in situ Fourier transform infrared spectrophotometric system in addition to a quartz crystal microbalance and quadrupole mass spectrometer. Contaminants can be collected and subjected to infrared spectroscopy at the collection temperature, circumventing problems associated with ex situ infrared measurements. Preliminary results indicate that VCM, with deposition thicknesses less than 200 Å, can be identified.		

CONTENTS

I.	INTRODUCTION.....	5
II.	INSTRUMENTATION.....	7
	A. Chamber.....	7
	B. Collection and Analysis Apparatus.....	9
	C. Temperature Controls.....	11
	D. Microcomputer Data Acquisition System.....	11
III.	EXPERIMENTAL.....	13
	A. Materials.....	13
	B. Procedure.....	13
IV.	RESULTS AND DISCUSSION.....	15
	A. Solithane 113/300.....	15
	B. 3M No. 465 Transfer Tape.....	18
	C. RTV 560.....	18
V.	CONCLUSIONS.....	25
VI.	REFERENCES.....	27

FIGURES

1.	Volatile Condensable Materials Facility.....	8
2.	VCM Facility, Optical Arrangement.....	10
3.	Solithane 113/300 Collected Mass Versus Time.....	16
4.	Solithane 113/300 VCM Infrared Spectra.....	17
5.	3M No. 465 Collected Mass Versus Time.....	19
6.	3M No. 465 VCM Infrared Spectra.....	20
7.	RTV 560 Collected Mass Versus Time.....	21
8.	RTV 560 VCM Infrared Spectra.....	22

I. INTRODUCTION

The current generation of satellites must carry out their missions with high reliability and for extended periods of time. As a result, stringent lifetime requirements are placed on satellite systems; these will become even more stringent with future generations of satellites. Contamination of critical satellite surfaces has long been recognized as a potential problem area. Problems can arise because sensitive surfaces can be coated by contaminants and because the molecular structures of such contaminants can be altered by interaction with the space environment. In addition, the presence of cryogenic satellite surfaces increases the potential for contamination because of the larger sticking coefficients of contaminants at low temperatures.

Until recently, there has been little work on identifying the chemical composition of volatile condensable materials (VCM) or on determining the changes that occur in VCM chemistry as a result of exposure to solar radiation or high-energy particles. Most VCM-related activities have involved materials screening procedures, such as the standardized ASTM VCM procedure,¹ and techniques used to determine solar absorptance values, e.g., reflectance and thermal measurements. These techniques are very useful and provide needed data for project planning purposes. They do not, however, contribute to the area of contaminant identification and environment-induced changes in contaminant molecular structure. Not until the actual contaminants are identified is it possible to recommend changes in material processing or selection that could help maximize the performance of satellite systems. Phillips et al.² recognized the need for research in this area. Using infrared spectroscopy, they observed changes in VCM that were brought about through exposure of the VCM to vacuum ultraviolet radiation. A disadvantage in their approach was that the VCM infrared spectra had to be taken ex situ and at room temperature. Although the VCM was collected at low temperature, no spectral information was obtained under the actual VCM collection conditions, and any changes that occurred in the VCM resulting from exposure of the material to ambient conditions could not be determined.

A new VCM facility has been constructed in response to the need for the identification of VCM and the determination of the changes that the contaminants undergo as the result of exposure to the orbital environment. A unique in situ Fourier transform infrared spectrophotometric system is incorporated into the facility. This facility is described, and some of the preliminary infrared and mass accumulation results are presented in this report.

II. INSTRUMENTATION

A. CHAMBER

The VCM chamber (Figure 1) is an oil-free stainless-steel tank that is pumped with a Balzers Model TSU 110 110 liter/sec turbomolecular pump and a Perkin Elmer/Ultex 100 liter/sec ion pump. Seals and joints are made with crushable copper gaskets and glass-to-metal seals. An adhesive, RTV 560 polysiloxane, is used to seal the entrance and exit potassium bromide (KBr) windows for the infrared system. No background contamination caused by outgassing of the window adhesive has been observed. Slip-on Teflon insulation is used on internal thermocouple wiring. A tubular cryoshield between the outgassing source and the collectors restricts the experiments to line-of-sight contaminant deposition.

The sample position is 7 in. from the detectors. For low outgassing materials, insufficient VCM would be deposited on the quartz crystal microbalance (QCM) and internal reflection element (IRE). In an attempt to increase the contaminant flux that impacts the collecting surfaces, a copper tube was attached to the sample holder. The tube is 0.43 in. diam and 5 in. long, so that it terminates 2 in. from the detectors. In this arrangement, the tube acts as a secondary source by channeling the VCM from the sample. Calculations of VCM flux distributions, performed following the experiments, indicate that the flux distribution was considerably more peaked along the axis of the tube than we had anticipated.³ Consequently, a VCM flux increase of only a factor of 2 to 3 at the detectors was realized relative to outgassing without the tube in place. In addition, there was a flux gradient across the QCM and IRE. Therefore, percent VCM values for comparison with NASA VCM values⁴ have not been calculated for this report. Efforts to increase the VCM flux at the collecting surfaces using well characterized source configurations are under way.

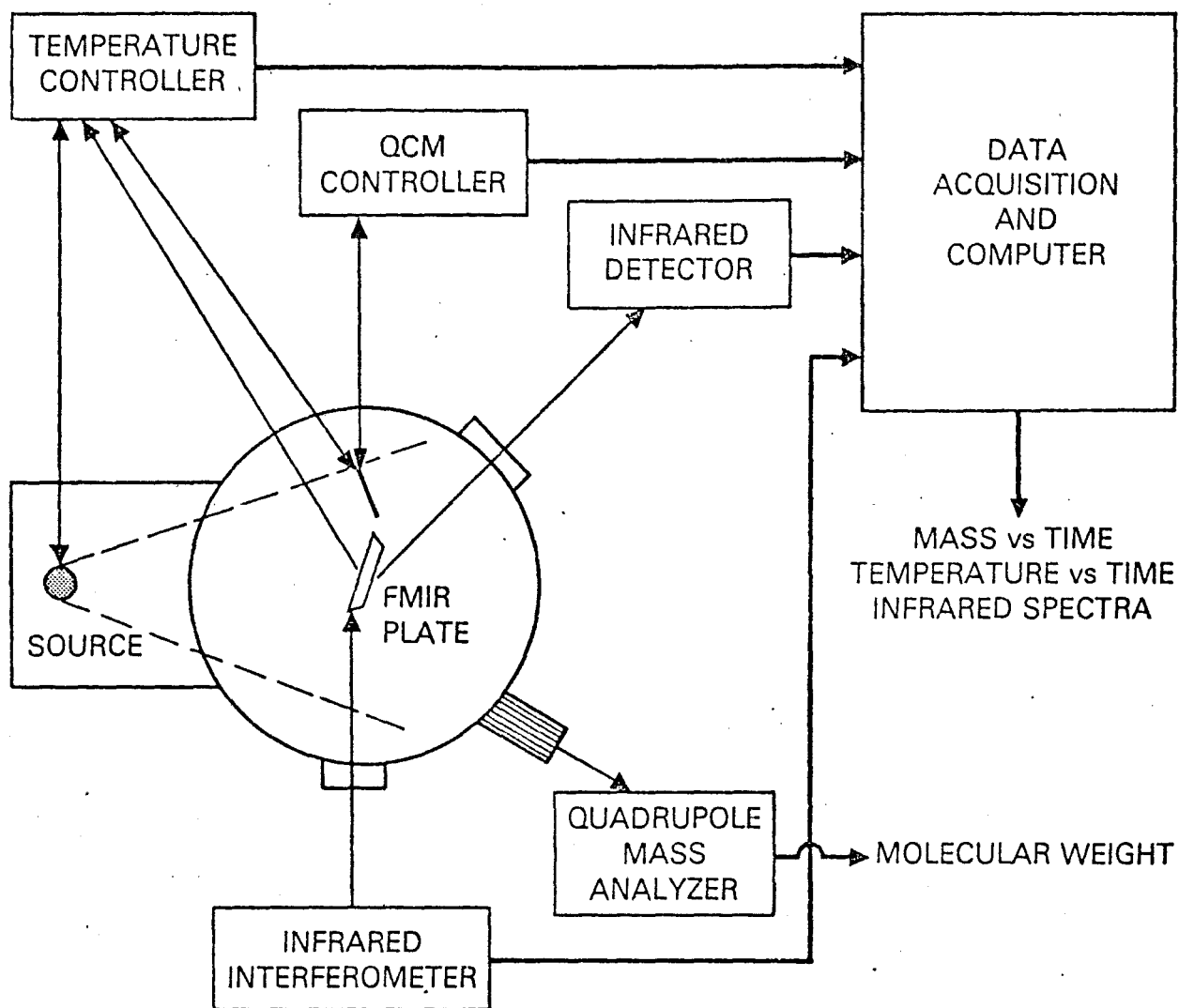


Figure 1. Volatile Condensable Materials Facility

B. COLLECTION AND ANALYSIS APPARATUS

1. FOURIER TRANSFORM INFRARED SPECTROPHOTOMETER SYSTEM

The infrared spectrophotometric system (Figure 2) is a modular system. Broadband radiation originates at a Perkin Elmer Globar infrared source, is collimated, and enters a Bloch Engineering Model 296 fast-scanning Michelson interferometer. The radiation emerges as a collimated train of interferogram pulses and is focused through the chamber KBr entrance window on the aperture of a 60-deg trapezoidal IRE. VCM, which has coated one surface of the IRE, is spectrally sampled by means of internal reflection spectroscopy.⁵ The radiation, which carries the sample spectral information, exits the IRE, passes through the KBr exit window, and is focused on an Infrared Associates HCT 16/18 mercury-cadmium-telluride detector. The interference data are stored on floppy disks and are later transformed into infrared spectra by means of a CDC 7600 computer. The IREs used are supplied by Harrick Scientific and are composed of either germanium or KRS-5. Temperature calibration of the IREs indicated that there was a large temperature gradient between the edge of the IRE where it contacted the holder and the center of the IRE. The temperature gradient results from poor thermal contact between the holder and the IREs. We are currently working to improve this condition.

2. QUARTZ CRYSTAL MICROBALANCE

Doublet crystals are used on the QCM, with the sensing and reference electrodes on the same 1.5×0.75 -in. crystal wafer of the type developed by Termeulen et al.⁶ The doublet crystals were used because temperature-induced beat frequency excursions were minimized with the reference and sensing crystals on the same wafer. We observed beat frequency shifts on the order of 30 to 40 Hz for the temperature range -105 to 25°C , which is in agreement with earlier work.²

The crystals were prepared by purchasing from Monitor Products 35-deg 10-min AT-cut crystals with platinum deposits in the desired electrode geometry. Either aluminum or gold was vacuum deposited over the platinum to provide the appropriate collecting surface. The resonance frequency of the crystals is

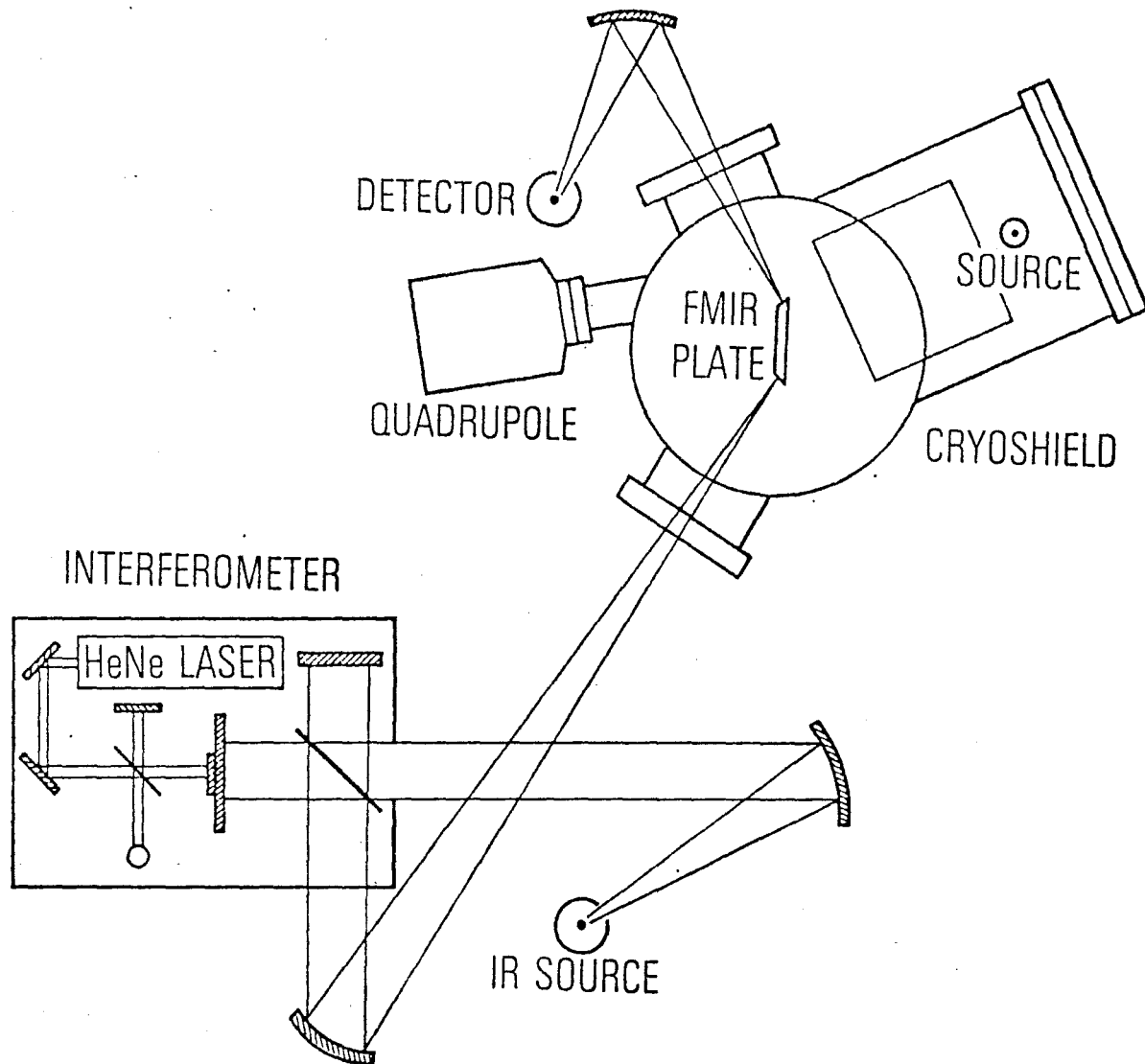


Figure 2. VCM Facility, Optical Arrangement

5 MHz. For our calculations of mass deposition, the theoretical value of $57.5 \text{ Hz cm}^2 \mu\text{g}^{-1}$ was used.⁷

The crystal wafers are mounted on an OFHC copper baseplate. Copper beryllium "fingers" hold the crystal suspended between the baseplate and the copper cover. Temperature equilibration of the wafer with the holder is accomplished by means of contact with the copper beryllium. Calibration of the QCM crystal temperature indicated that at holder temperatures lower than -150°C , the center of the crystal was 6 deg warmer than the holder. This temperature difference was smaller at higher temperatures. The front cover is designed so that only the sensing side of the wafer is exposed during operation, i.e., the reference side is masked.

3. RESIDUAL GAS ANALYZER

An EAI Model 250 quadrupole mass spectrometer is interfaced to the system for mass analysis of outgassed material.

C. TEMPERATURE CONTROLS

The outgassing source temperature range is from -196 to greater than 200°C . Cooling is only required during initial pumpdown and is accomplished by filling a reservoir attached to the source holder with liquid nitrogen (LN_2). Heating is accomplished with a cartridge heater regulated with a Variac. The QCM and IRE holders are cooled with LN_2 . The QCM and IRE temperatures are controlled by Omega Model 50 temperature controllers. The cold shroud is maintained at low temperature by constant contact with a reservoir of LN_2 . Copper-constantan thermocouples are used to monitor the source, IRE, QCM, and cold-shroud temperatures. The thermocouples are referenced to 0°C electronically.

D. MICROCOMPUTER DATA ACQUISITION SYSTEM

Frequency data from the QCM and temperature data for the IRE, QCM, source, and cold shroud are continuously acquired by a microcomputer and stored on floppy disks. The sampling interval can be varied from one second to one day. However, 10-min intervals are adequate for most experiments. The data can be displayed on a terminal concurrent with floppy disk storage during periods when a printed or visual record is desirable.

The microcomputer also controls the pulse frequency of the interferometer during infrared spectral measurements, acquires the digital interferograms, co-adds the interferograms, and stores them on floppy disks. Between 80 and 160 separate interferograms are routinely co-added to obtain adequate signal-to-noise levels.

III. EXPERIMENTAL

A. MATERIALS

Samples of Solithane 113/300 polyurethane adhesive, 3M No. 465 acrylic transfer tape, and RTV 560 polymethylphenylsiloxane were received from a subcontractor for analysis. The materials were not preconditioned for temperature and humidity prior to installation in the facility.

B. PROCEDURE

The sample material (VCM source) was initially weighed, placed in position on the sample holder, and installed in place in the chamber. Pumping the chamber for 15 min with the turbomolecular pump reduced the chamber pressure to approximately 1×10^{-5} Torr. At a chamber pressure of approximately 1×10^{-4} Torr, the source and the shroud were cooled to -196°C to prevent premature outgassing of the sample. When the chamber pressure was 1×10^{-5} Torr or less, the ion pump was turned on and the turbomolecular pump was valved off from the system. The IRE and QCM were cooled to their respective temperatures, and low-temperature background infrared spectra were taken. The temperatures of the QCM and IRE stabilized at -97 and -100°C , respectively, in approximately 30 min, after which the sources were adjusted to their operating temperatures (125°C for Solithane 113/300 and 3M No. 465 and 20°C for RTV 560) and outgassing was begun. For collector temperature in the range of -100°C and chamber pressures of approximately 1×10^{-8} Torr, water vapor or other atmospheric gases that may be emitted from the sources will not condense, but almost any outgassed organic species will be collected. Previous experiments indicated that considerable quantities of water were collected on the IRE when its temperature was colder than -130°C .

Temperatures and QCM frequencies were acquired at 10-min intervals during the course of the experiments. Infrared spectra were taken daily as the VCM was being collected. The experiments lasted from 6 to 10 days.

The experiments were terminated by cooling the sample to room temperature and permitting the QCM to warm at a predetermined rate so that desorption

information could be obtained. After the QCM reached ambient temperature, first the IRE and then the shroud were permitted to warm to ambient temperature. The pumps were turned off, and the chamber was backfilled with dry nitrogen.

Between experiments, the chamber and ion pump were baked out for at least 24 hr. Background contamination was determined to be negligible by operating the system without a sample present.

IV. RESULTS AND DISCUSSION

A. SOLITHANE 113/300

Collected mass-versus-time data for Solithane 113/300 are shown in Figure 3. The approximately $2.0 \mu\text{g cm}^{-2}$ VCM that was collected over 180 hr translates into a thickness of 200 Å on the IRE if a density of 1.0 is assumed for the VCM.

The VCM desorption data in Figure 3 indicate that the VCM began to desorb from the QCM when the QCM temperature reached -62°C . As the QCM temperature approaches room temperature, the mass reading apparently goes below zero. This behavior is a manifestation of a temperature-dependent frequency response of the QCM, i.e., the beat frequency of the QCM changes by 30 to 40 Hz (0.5 to $0.7 \mu\text{g cm}^{-2}$) when the QCM temperature changes from -97 to 20°C . The zero mass reading was established with the QCM at -97°C . Less than $0.2 \mu\text{g cm}^{-2}$ remained when the QCM reached ambient temperature. (Because of fluctuations in the QCM frequencies, our accuracy is limited to $\pm 0.2 \mu\text{g cm}^{-2}$.) This mass loss when the IRE warms to room temperature emphasizes the importance of performing spectral measurements at the collection temperature.

The infrared spectra of the collected VCM are shown in Figure 4. The only outstanding feature in these spectra is the strong absorption at 2250 cm^{-1} . There are very few functional groups that absorb in this region. This absorption undoubtedly corresponds to the isocyanate functional group, $-\text{N} = \text{C} = \text{O}$. Solithane 113/300 is a polyurethane polymer, and one of the precursor molecules is an aromatic diisocyanate. Typical aromatic diisocyanate spectra⁸ exhibit an approximately 2250 cm^{-1} absorption that is the most prominent feature in the spectra. In our experimental spectra, possible C-H and C-C absorption features are apparent but are not significantly above the noise level. The spectra in Figure 4 correspond to maximum contaminant thicknesses of 150 and 200 Å. The thicknesses may be much less because of the temperature gradient across the IRE.

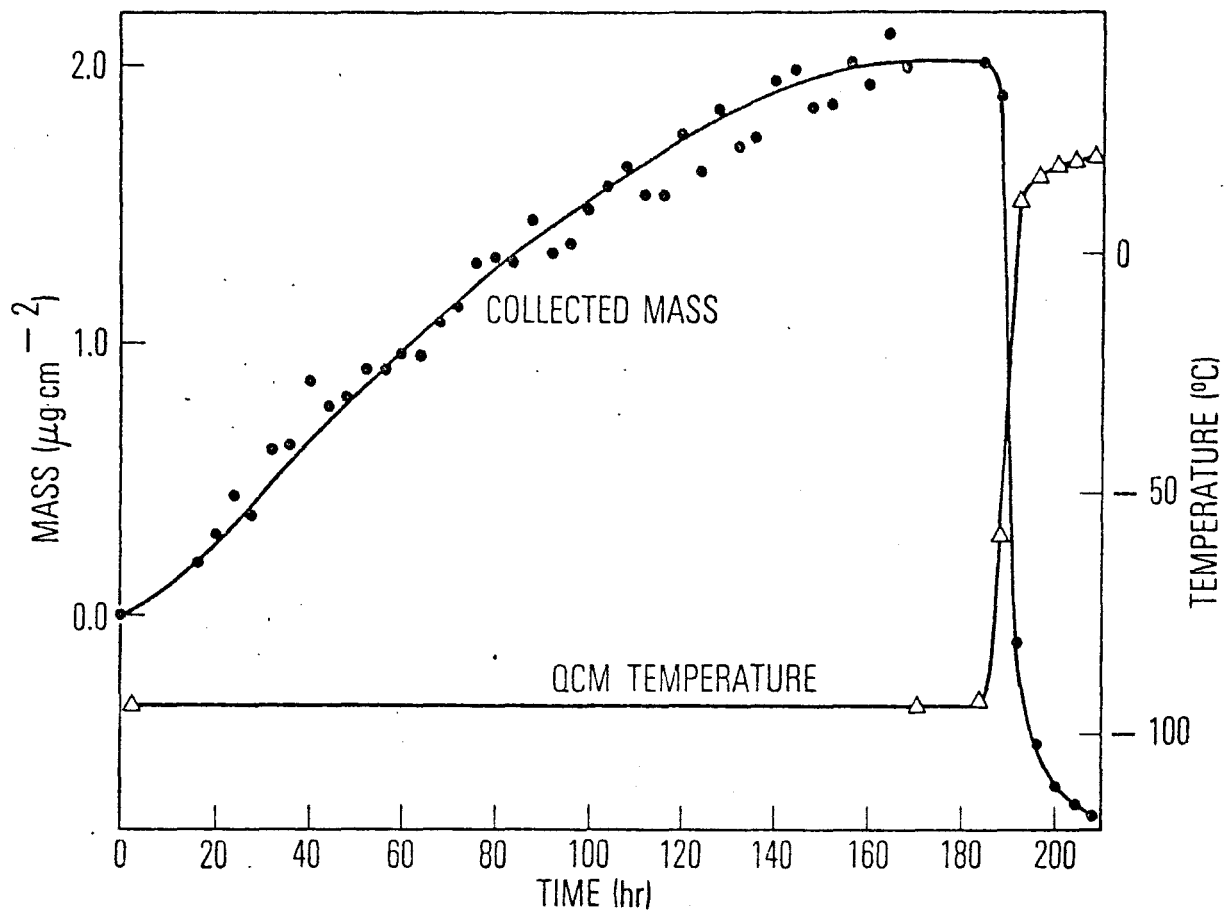


Figure 3. Solithane 113/300 Collected Mass Versus Time

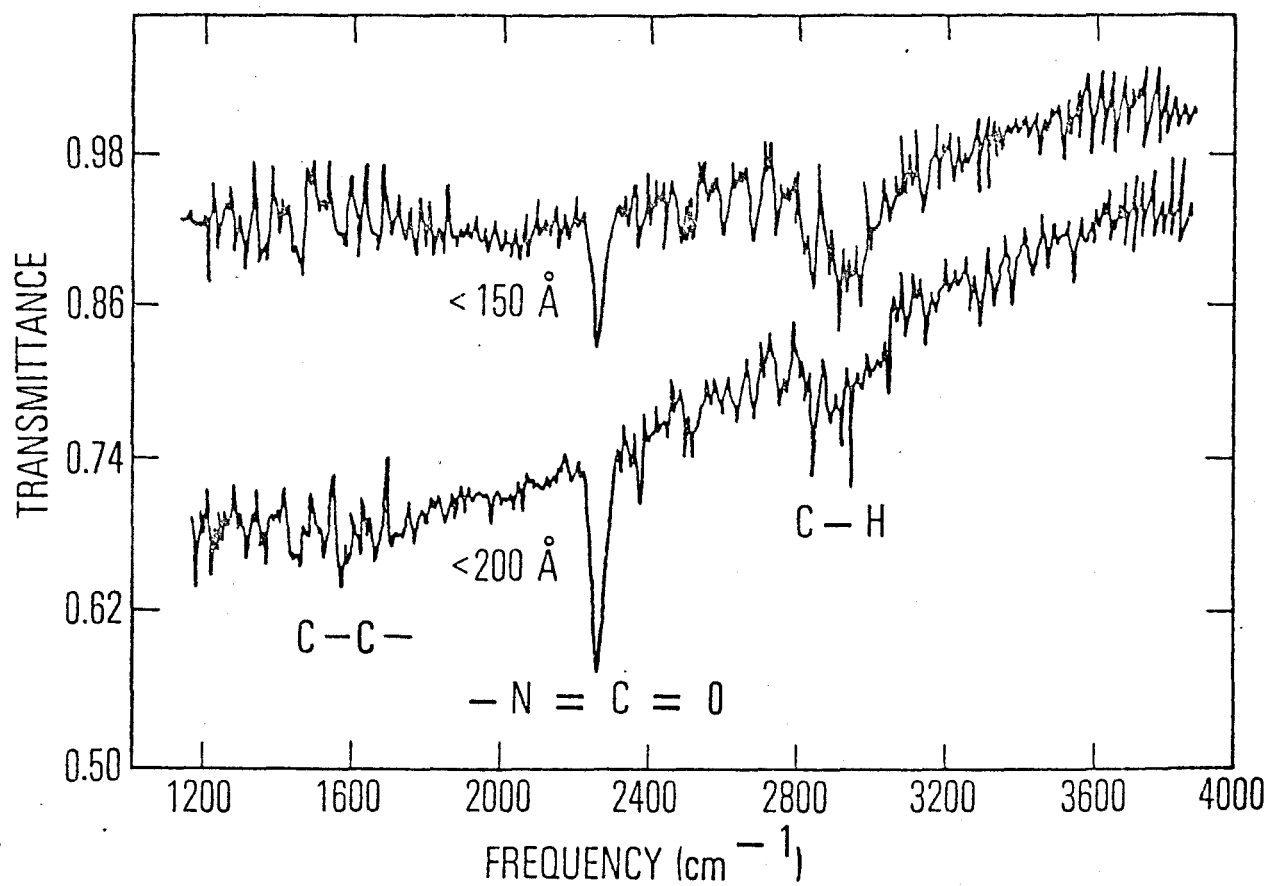


Figure 4. Solithane 113/300 VCM Infrared Spectra

B. 3M No. 465 TRANSFER TAPE

Collected mass-versus-time data for 3M No. 465 transfer tape are shown in Figure 5. The collected mass value after 160 hr was approximately $2.4 \mu\text{g cm}^{-2}$. This value corresponds to a VCM deposition of 240 \AA on the IRE.

The desorption data, Figure 5, indicate that the VCM began to desorb when the QCM temperature was higher than -70°C . The mass loss stops when the QCM temperature is maintained at -63°C , and the collected mass decreases very little until resumption in the warming of the QCM. The desorption continues for approximately 20 hr while the QCM is warming up. The initial desorption is caused by either a frequency shift resulting from a change in the QCM temperature or the desorption of highly volatile VCM components. The observation that the mass value levels off at -63°C is consistent with both explanations. As the temperature of the QCM increases above -63°C , the VCM desorption rate is not consistent with the desorption of one component, but is consistent with the desorption of several components, i.e., the rate remains fairly low despite a QCM temperature increase of approximately 60°C .

The infrared data, Figure 6, exhibit only C-H absorption. No carbonyl absorption is present. These data suggest that the VCM is a hydrocarbon and is not composed of acrylate monomers that have outgassed.

C. RTV 560

For RTV 560, the collected mass-versus-time data are given in Figure 7. The results were surprising. With the sample at approximately 20°C , the outgassing was linear with time and resulted in the collection of approximately $18 \mu\text{g cm}^{-2}$ after 50 hr. The sample was cooled to -196°C after 35 hr, because we were concerned that the QCM would become saturated. The high level of outgassing indicates that the material may have been improperly cured. After the system was maintained with the source cold for approximately 50 hr, the microcomputer malfunctioned and the capability to acquire infrared, QCM, and temperature data was lost.

The infrared spectra, Figure 8, were taken with estimated sample thicknesses of 460 to 1800 \AA before the computer malfunctioned. The outstanding

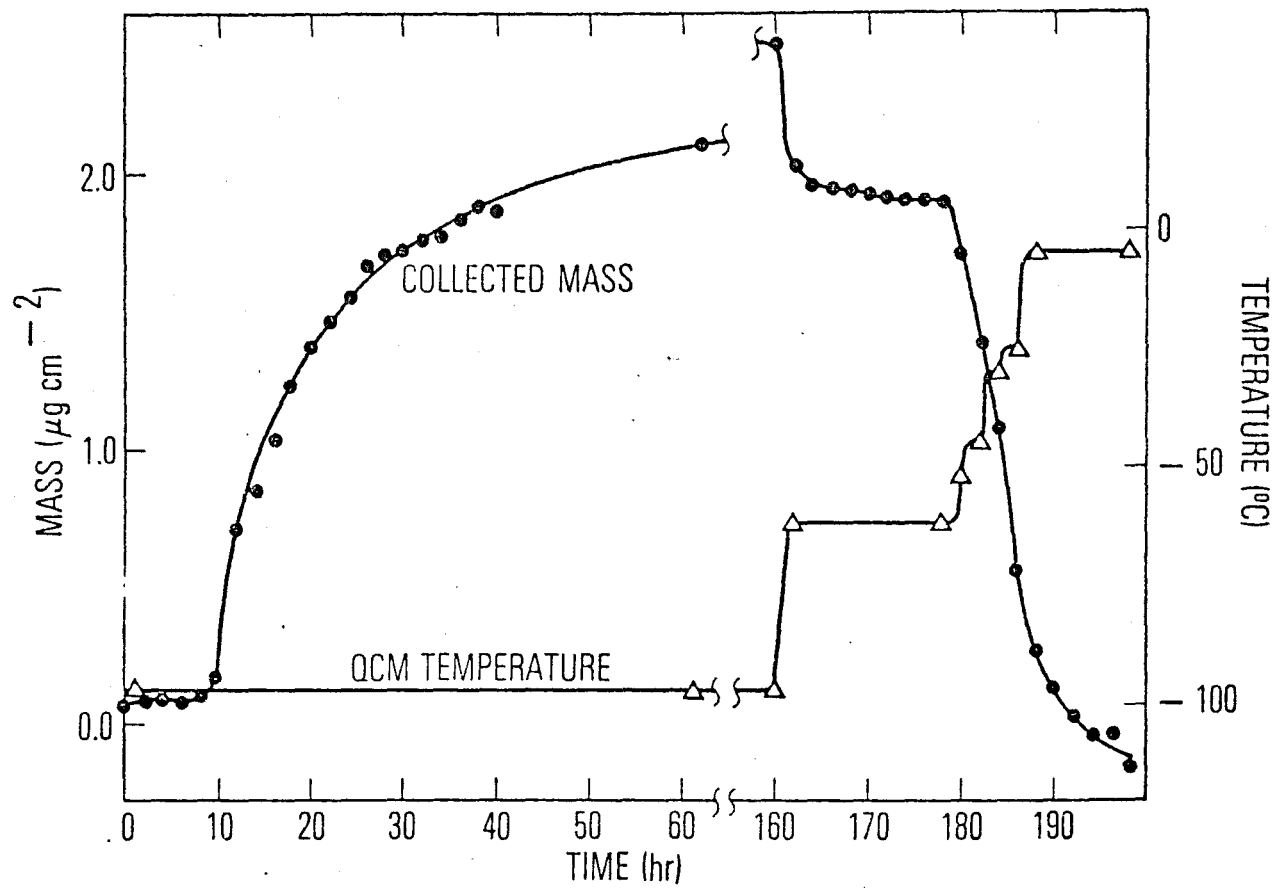


Figure 5. 3M No. 465 Collected Mass Versus Time

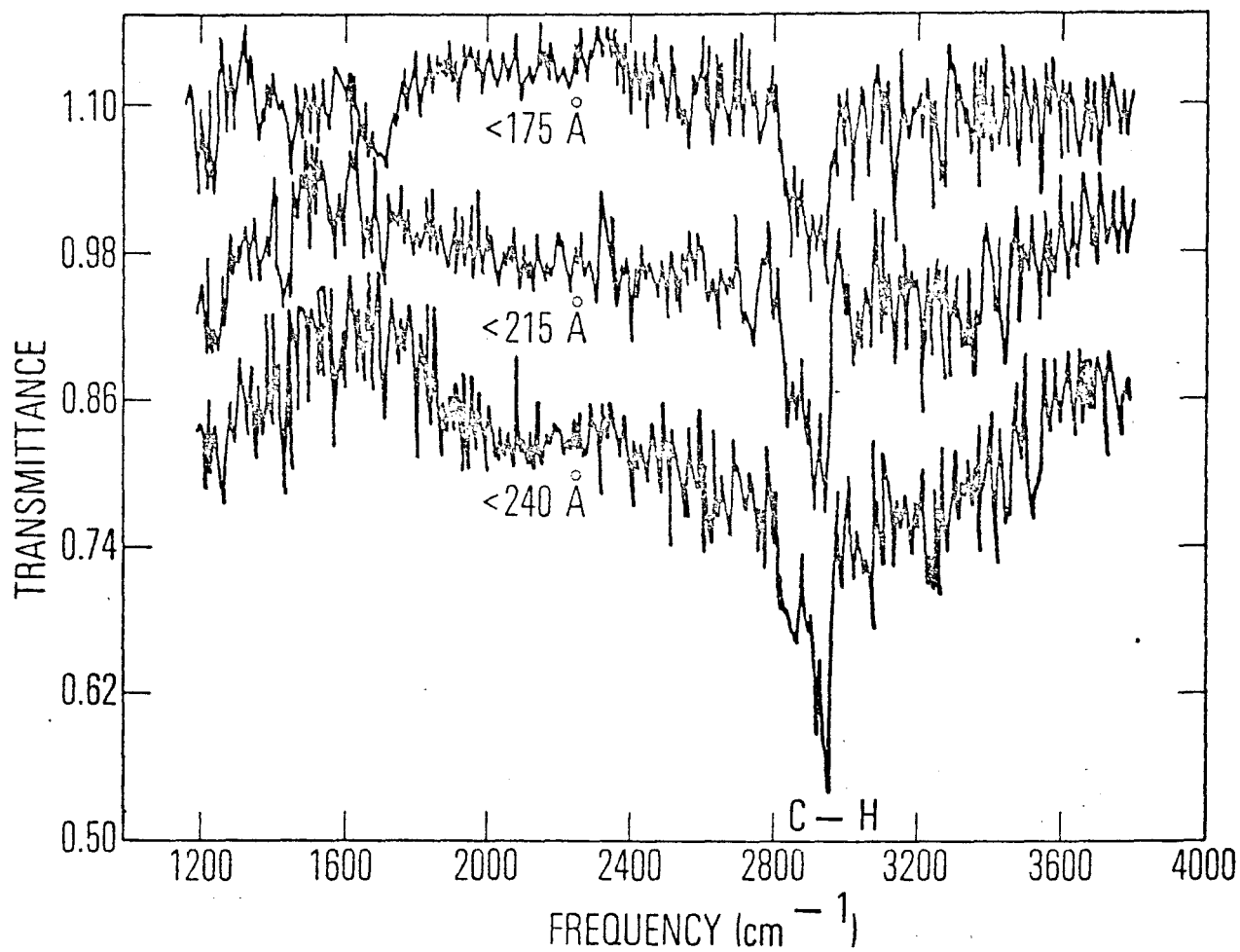


Figure 6. 3M No. 465 VCM Infrared Spectra

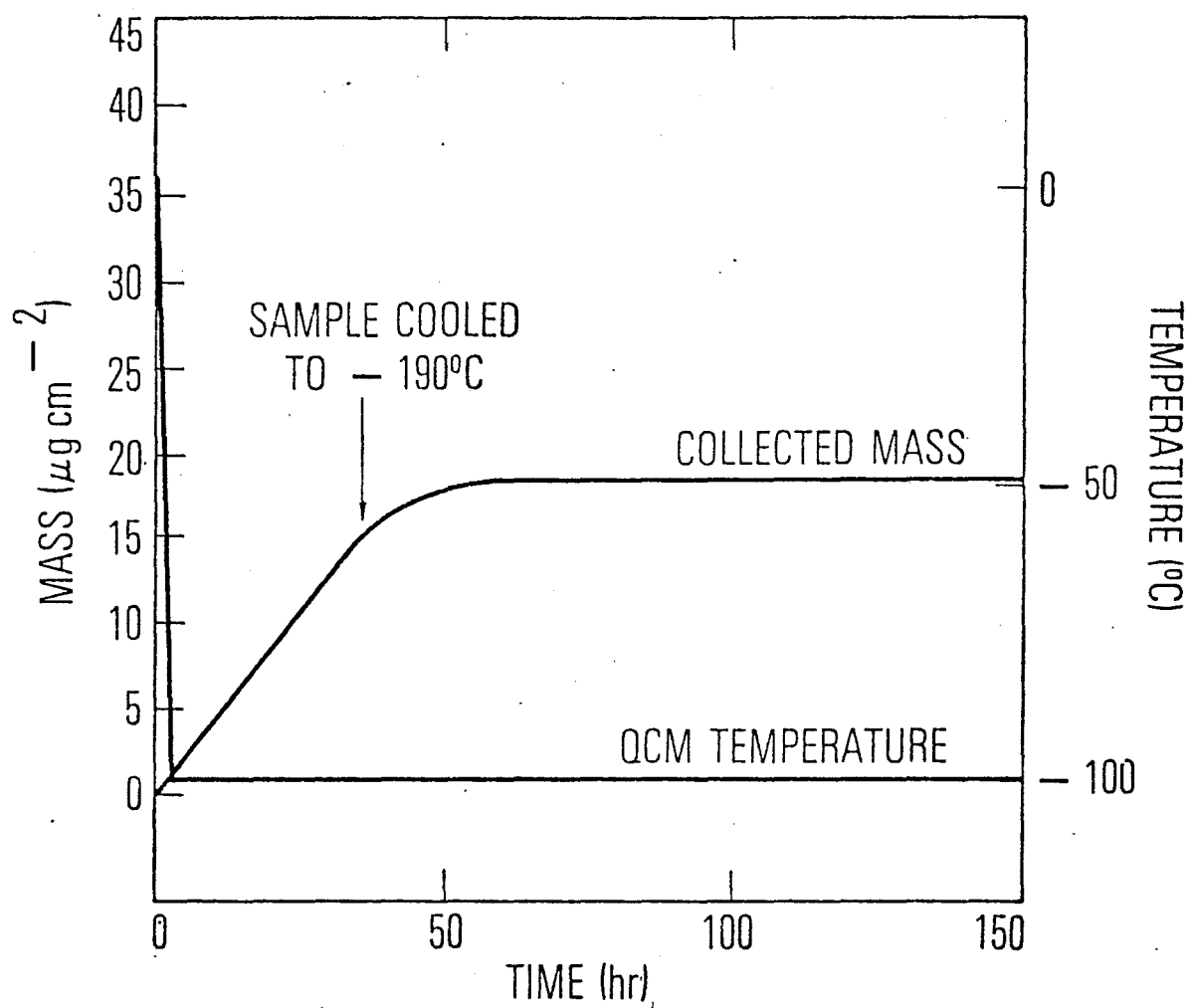


Figure 7. RTV 560 Collected Mass Versus Time

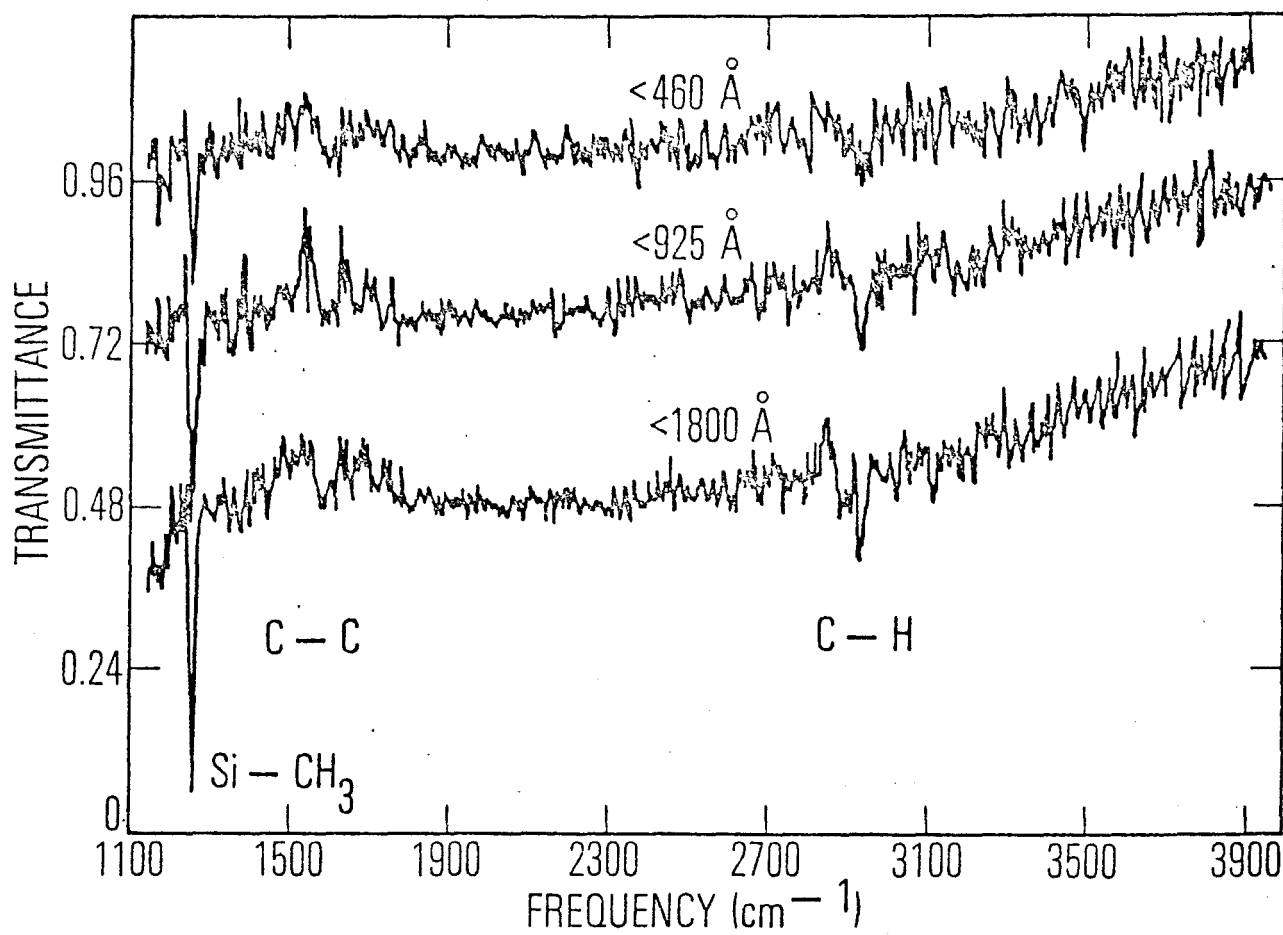


Figure 8. RTV 560 VCM Infrared Spectra

feature in the spectra is the strong absorption at approximately 1250 cm^{-1} characteristic of the Si-CH₃ bond.^{9,10} This feature and the C-H absorption at approximately 2940 cm^{-1} identify the VCM as a methyl siloxane. There is no evidence of phenyl siloxane absorption in the spectra. Thus, although RTV 560 is a mixed methyl-phenyl siloxane, only the methyl siloxane outgasses in significant quantities.

V. CONCLUSIONS

The conclusions from the preliminary experiments with the VCM facility are the following:

1. Because of the low desorption temperatures of the VCM, low-temperature collection and in situ spectroscopy of VCM is superior to ex situ spectroscopy techniques. The in situ technique circumvents problems associated with sample removal and exposure to the ambient environment.
2. Contaminants with strong infrared transitions can be identified with less than 200 Å of deposit on the IRE. For the materials in this study, the prominent absorptions at 3.4, 4.4, and 7.9 μm would be significant if they occurred in important band-pass regions for spacecraft optical devices. In such a case, specific care to prevent contamination must be exercised.
3. The VCM deposits for all three materials desorb completely when the QCM is warmed. The desorption occurs well below room temperature. Data for room-temperature collection⁴ indicate substantial quantities of VCM. Apparently, the VCM is being fixed by reactions that occur rapidly at room temperature, e.g., polymerization,¹¹ but are not important at lower temperatures. The VCM materials would present a problem in cryogenic optics and surfaces because of large sticking coefficients at cryogenic temperatures.
4. The VCM facility with in situ infrared spectroscopy capability has been demonstrated to be useful for the identification and quantification of outgassed materials.

VI. REFERENCES

1. "Standard Test Method for Total Mass Loss and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment," ANSI/ASTM E 595-77, American Society for Testing and Materials, Philadelphia, Pennsylvania.
2. Phillips, R. W., L. U. Tolentino, and S. Feuerstein, "Spacecraft Contamination Under Simulated Orbital Environment," J. Spacecr. Rockets, Vol. 14, p. 501. 1977.
3. Giordmaine, J. A., and T. C. Wang, J. Appl. Phys., Vol. 31, p. 463. 1960.
4. "Compilation of VCM Data of Non-Metallic Materials," NASA JSC Houston, May 1979, Rev 21.
5. Harrick, N. J., Internal Reflection Spectroscopy, Interscience, 1967.
6. Termeulen, J. P., et al., Progress in Vacuum Microbalance Techniques, Vol. I, T. Gast and E. Robens, eds., Heyden 1972, p. 41.
7. Niedermayer, R., N. Gladkick, and D. Hillecke, Vacuum Microbalance Techniques, Vol. 5, K. H. Behrndt, ed., Plenum, 1966, p. 217.
8. The Coblentz Society Desk Book of Infrared Spectra, C. D. Craver, ed., The Coblentz Society, 1977.
9. Haslam, J., H. A. Willis, and D. C. M. Squirrel, Identification and Analysis of Plastics, 2nd ed., Butterworth, 1972.
10. Smith, A. L. Spectrochimica Acta, Vol. 16, p. 87. 1960.
11. Muraca, R. F., "Space Environment Effects on Polymeric Materials," Stanford Research Institute Project No. PLU 4257, 8 Dec. 1963.

LABORATORY OPERATIONS

The Laboratory Operations of The Aerospace Corporation is conducting experimental and theoretical investigations necessary for the evaluation and application of scientific advances to new military space systems. Versatility and flexibility have been developed to a high degree by the laboratory personnel in dealing with the many problems encountered in the nation's rapidly developing space systems. Expertise in the latest scientific developments is vital to the accomplishment of tasks related to these problems. The laboratories that contribute to this research are:

Aerophysics Laboratory: Launch vehicle and reentry aerodynamics and heat transfer, propulsion chemistry and fluid mechanics, structural mechanics, flight dynamics; high-temperature thermomechanics, gas kinetics and radiation; research in environmental chemistry and contamination; cw and pulsed chemical laser development including chemical kinetics, spectroscopy, optical resonators and beam painting, atmospheric propagation, laser effects and countermeasures.

Chemistry and Physics Laboratory: Atmospheric chemical reactions, atmospheric optics, light scattering, state-specific chemical reactions and radiation transport in rocket plumes, applied laser spectroscopy, laser chemistry, battery electrochemistry, space vacuum and radiation effects on materials, lubrication and surface phenomena, thermionic emission, photosensitive materials and detectors, atomic frequency standards, and bioenvironmental research and monitoring.

Electronics Research Laboratory: Microelectronics, GaAs low-noise and power devices, semiconductor lasers, electromagnetic and optical propagation phenomena, quantum electronics, laser communications, lidar, and electro-optics; communication sciences, applied electronics, semiconductor crystal and device physics, radiometric imaging; millimeter-wave and microwave technology.

Information Sciences Research Office: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, and microelectronics applications.

Materials Sciences Laboratory: Development of new materials: metal matrix composites, polymers, and new forms of carbon; component failure analysis and reliability; fracture mechanics and stress corrosion; evaluation of materials in space environment; materials performance in space transportation systems; analysis of systems vulnerability and survivability in enemy-induced environments.

Space Sciences Laboratory: Atmospheric and ionospheric physics, radiation from the atmosphere, density and composition of the upper atmosphere, aurorae and airglow; magnetospheric physics, cosmic rays, generation and propagation of plasma waves in the magnetosphere; solar physics, infrared astronomy; the effects of nuclear explosions, magnetic storms, and solar activity on the earth's atmosphere, ionosphere, and magnetosphere; the effects of optical, electromagnetic, and particulate radiations in space on space systems.